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(54) Mass spectra analysis of gases

(57) Mass spectra analysis of gases supplied simultaneously or sequentially in a carrier gas to the spectrometer where a first component of the gases has a different volume ratio with respect to the carrier compared to a second component is characterised by decreasing the concentration of the component with the larger volume ratio by an additional supply of carrier gas thereto. Apparatus operating on the "open split" system and characterised by provision of an additional diluting line for the carrier gas is also disclosed.

GB 2 273 561 A

FIG. 1

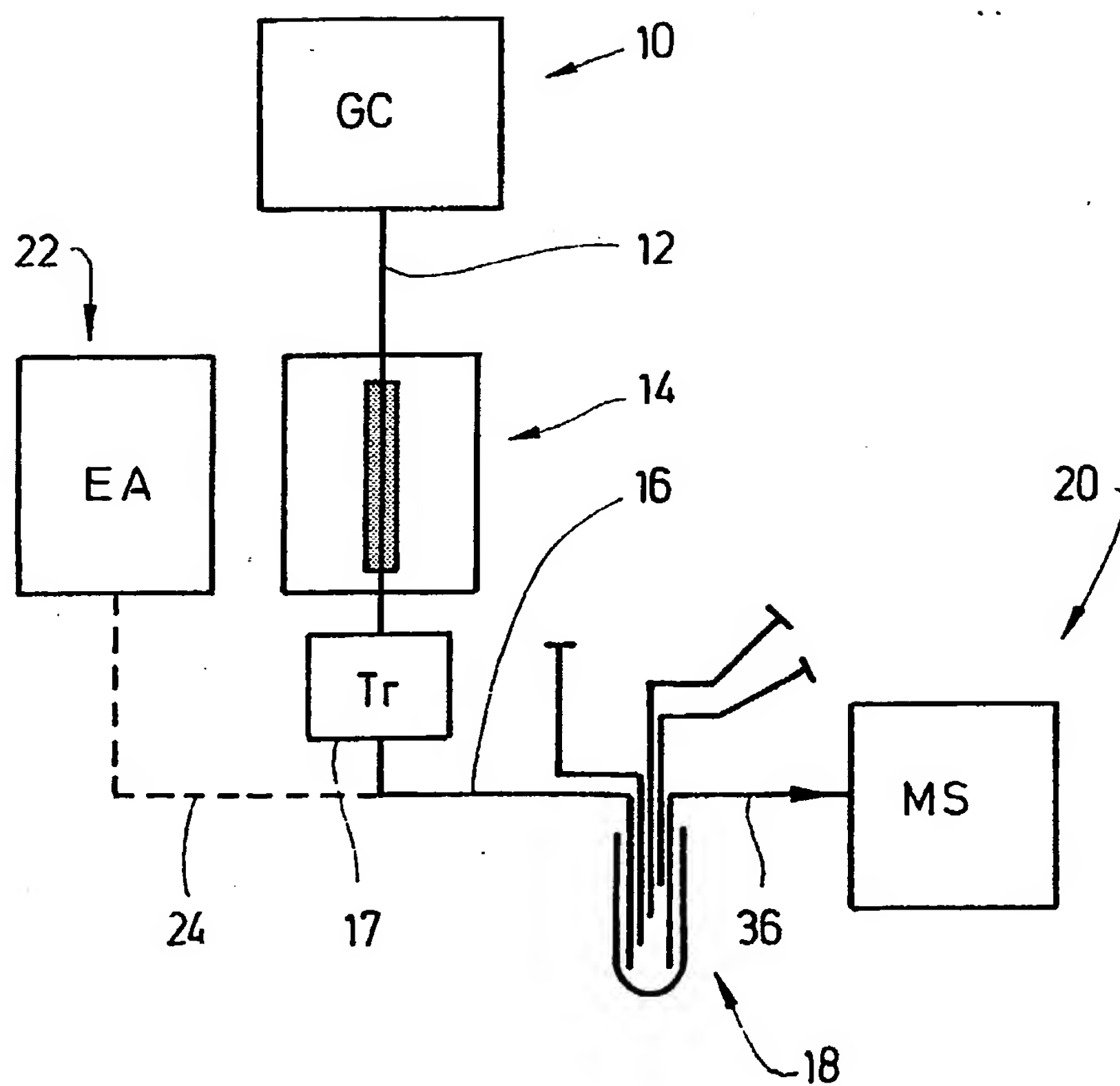


FIG. 2

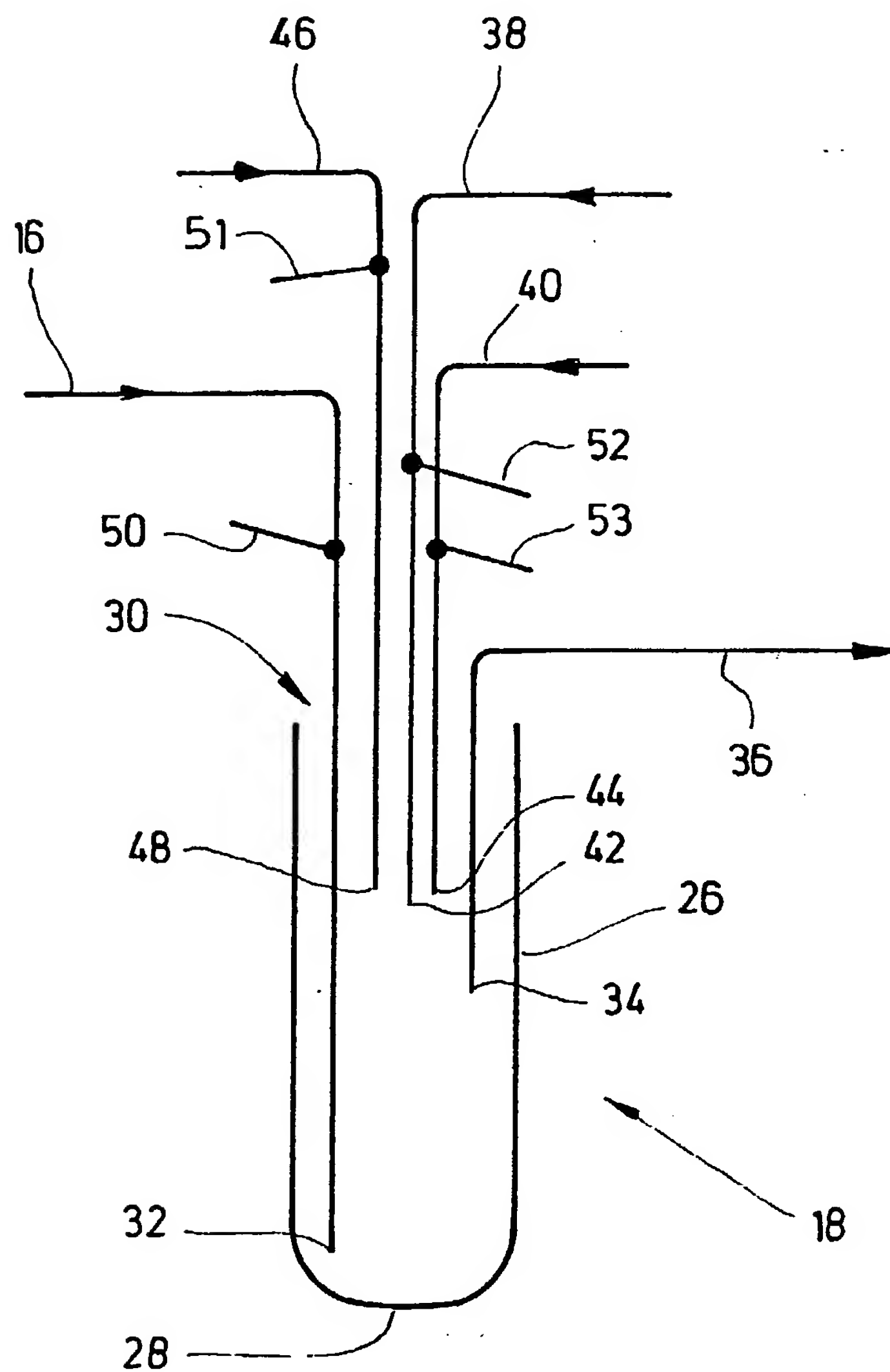


FIG. 3

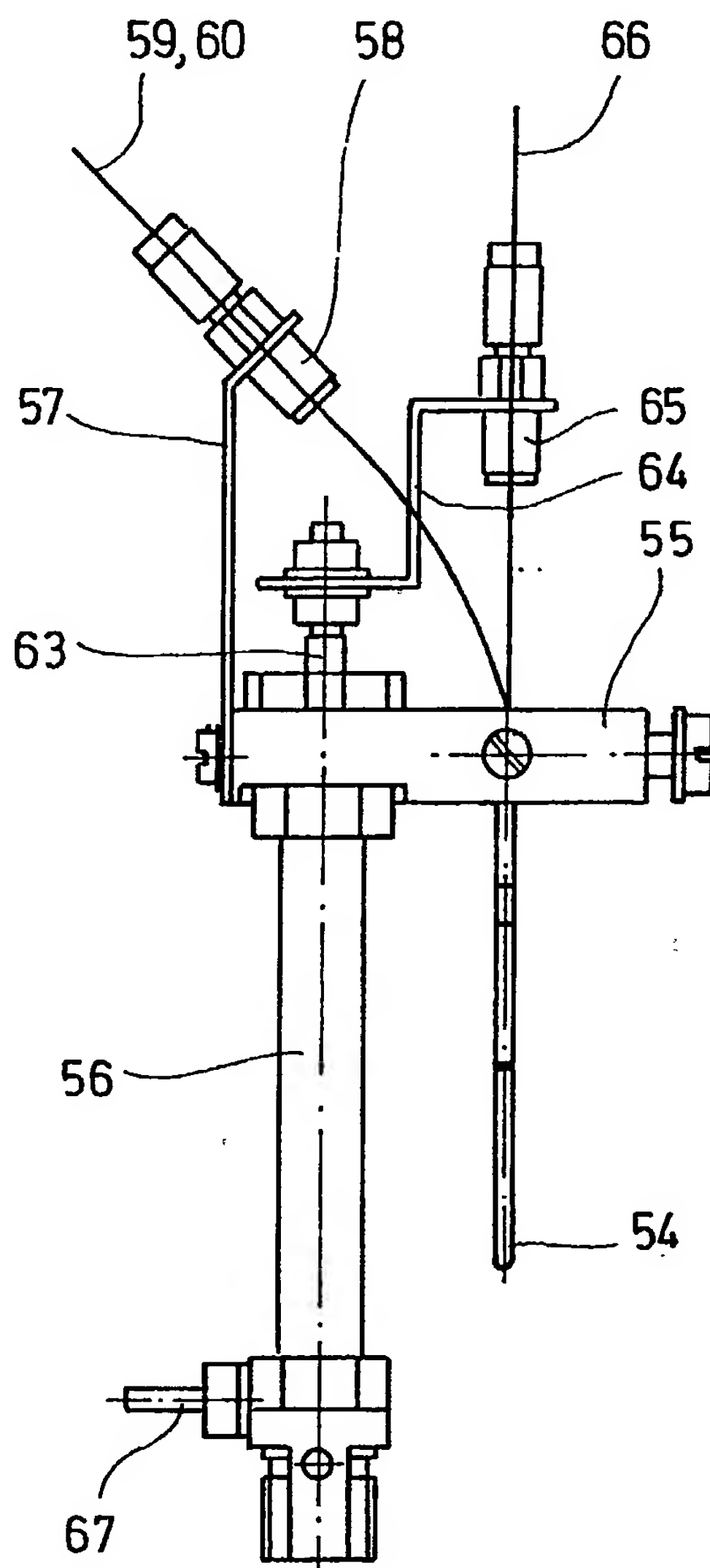


FIG. 4

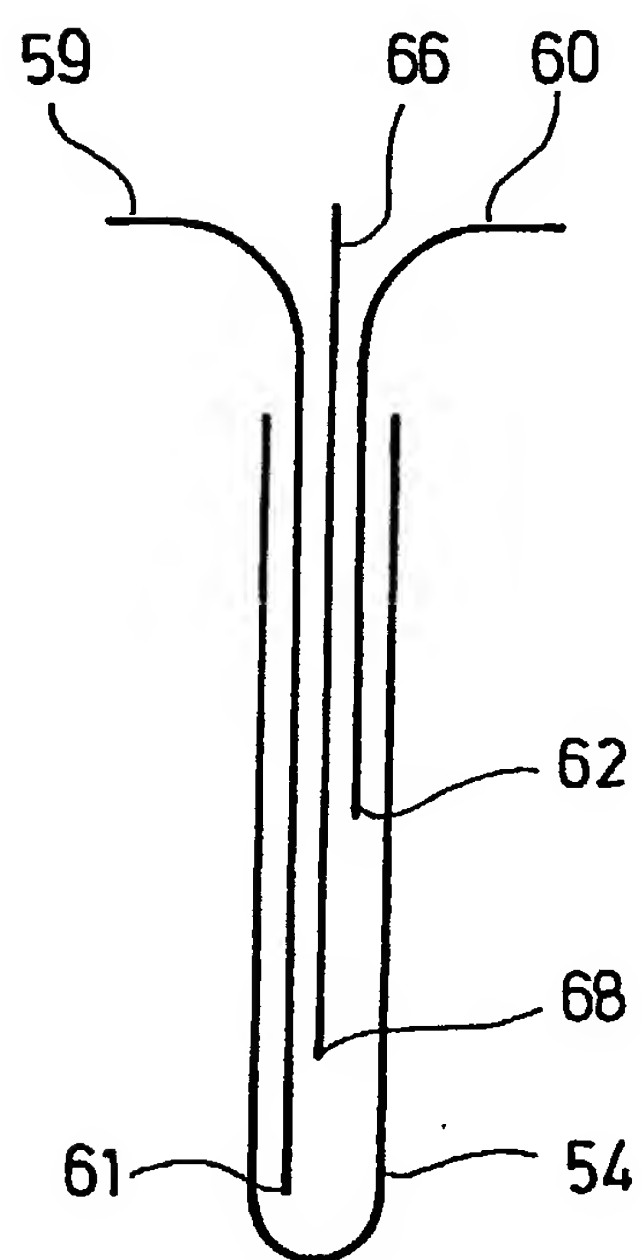


FIG.5

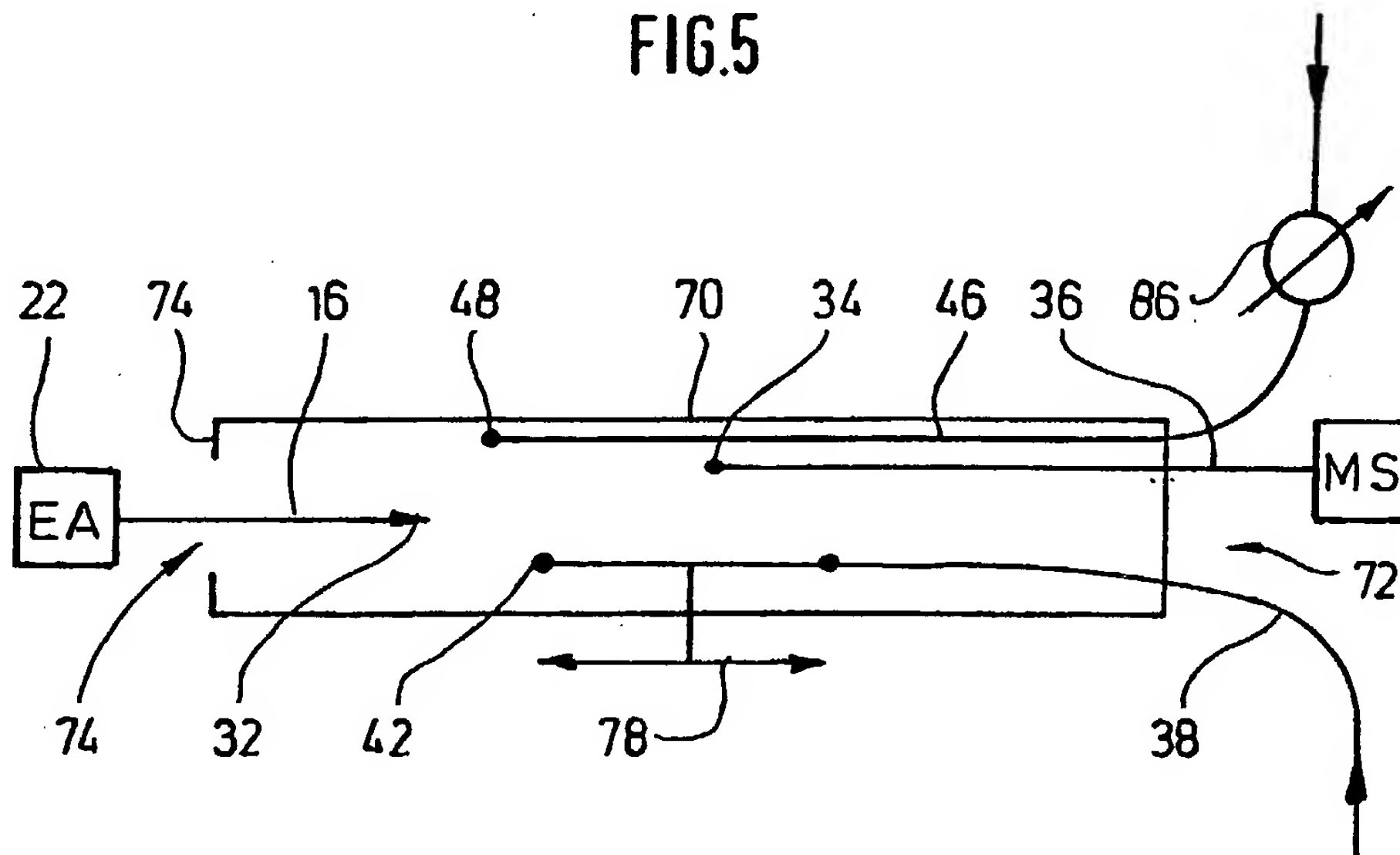
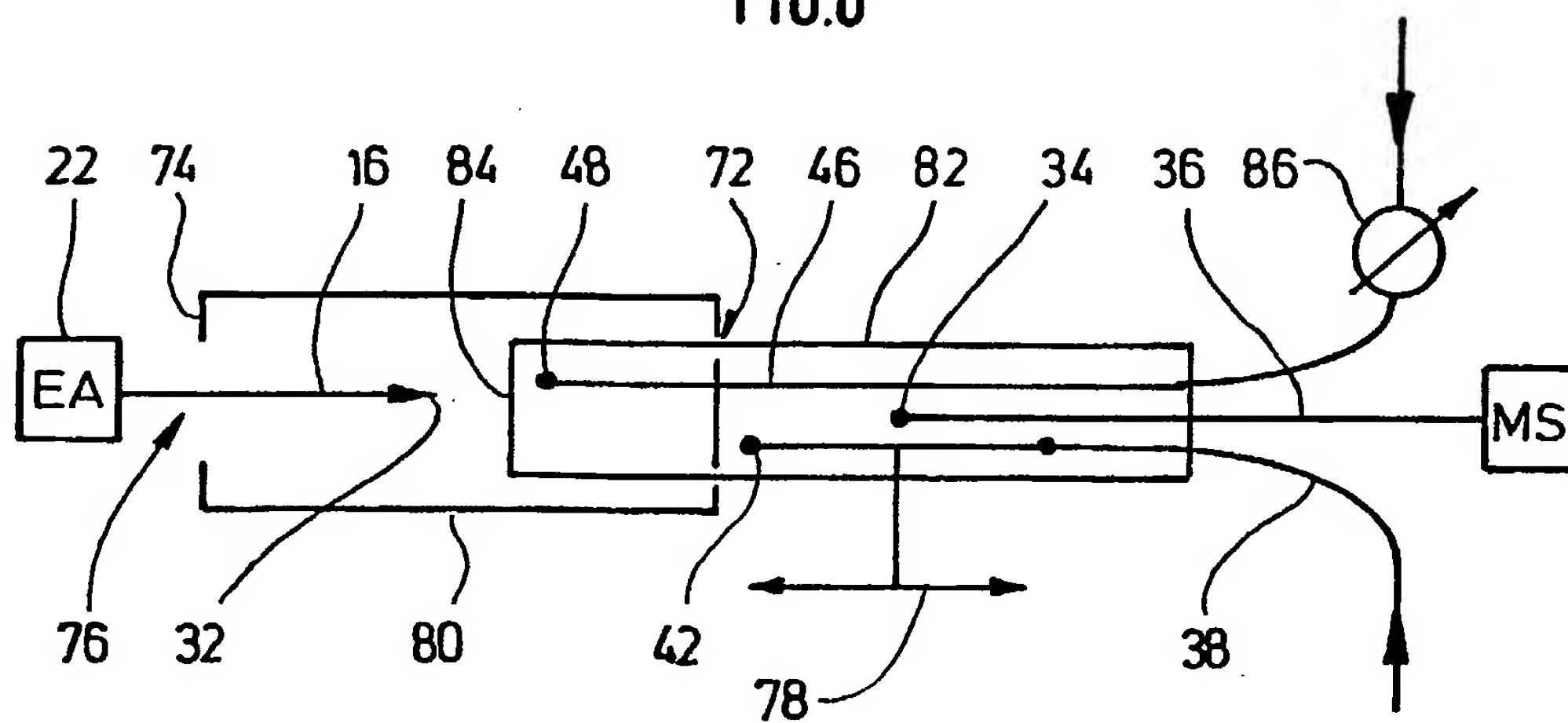


FIG.6



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Process for the analysis of gaseous components by mass  
spectrometry

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D e s c r i p t i o n :

1 The invention relates to a process for the analysis of  
several, especially two, gaseous components by mass  
spectrometry, the components being supplied, simultaneously  
or successively, with a carrier gas to a mass spectrometer,  
5 the first component having a different volume ratio  
relative to the carrier gas compared to the second  
component. Furthermore, the invention relates to an  
apparatus for the provision of gaseous samples for an  
analysis by mass spectrometry, especially for conducting  
10 the process.

Background of the invention and its preferred field of  
application is the isotope-ratio analysis by mass  
spectrometry, especially of carbon and nitrogen or, for  
example, of sulphur. In the course of a so-called  
GC-IRMS-analysis, for example, organic compounds or

1 compound mixtures can be separated in a gas chromatograph  
(GC) and the separated components can be decomposed in a  
downstream combustion oven. If the organic compound or the  
compound mixture contains carbon, hydrogen and nitrogen,  
5  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  are formed in the combustion oven by  
oxidation. In this case, it is relevant to determine the  
isotope ratios  $\text{C}^{12}/\text{C}^{13}$  of the  $\text{CO}_2$  and  $\text{N}^{14}/\text{N}^{15}$  of the  $\text{N}_2$ .  
This is attained by means of the downstream mass  
spectrometer, the sample gases  $\text{CO}_2$  and  $\text{N}_2$  being allowed to  
10 flow in on-line into the ion source of the mass  
spectrometer. The principle of the method is described, for  
example, in Analytical Chemistry, Vol. 50, Nr. 11,  
September 1978, pages 1465-1473 and in Org. Chem., Vol 16,  
Nr. 5-6, pages 1115-1128. Sometimes this analytical method  
15 is also abbreviated IRM-GCMS. Utmost precision is required  
in such analyses. In order to attain the required  
precision, the sample gases ( $\text{CO}_2$  and  $\text{N}_2$ ) are allowed to  
reciprocally flow into the mass spectrometer with a  
standard gas of which the isotope ratio is known. In the  
20 measurements, only the deviation of the isotope ratio of  
the sample relative to the standards is important. The  
deviations may be extremely small.

During a measurement, alternately  $\text{CO}_2$  or  $\text{N}_2$  and  
25 corresponding reference gases, i.e.  $\text{CO}_2$  and  $\text{N}_2$  having a  
standard isotope ratio, are supplied to the mass  
spectrometer. Normally, the quantity of  $\text{CO}_2$  produced in the  
analysis of organic compounds is much higher than the  
quantity of  $\text{N}_2$  (20:1 to 50:1). If the gases were allowed to  
30 flow into the MS in this ratio of concentration, ion  
currents of very different sizes would be generated for  $\text{CO}_2$   
and  $\text{N}_2$ . A mass spectrometer, however, operates at its  
optimum only in a certain range of ion current. It is,  
therefore, expedient to adjust the ion currents to one  
35 another. This can not be achieved by simply reducing the  
gas inflow of  $\text{CO}_2$ , for example by means of a throttle  
valve. A change in the throttling of the gas inflow always  
causes a change (even if only a small one) of the isotope

1 ratio (fractionation). A further problem arises: carrier  
gas (preferably helium) flows into the mass spectrometer  
together with the sample gas. The concentration of the  
carrier gas is substantially higher than that of the sample  
5 gas. This carrier gas is ionized in the ion source of the  
mass spectrometer together with the sample gas and produces  
a relatively high volume charge. As a change in the  
throttling of the gas inflow equally affects sample gas and  
carrier gas, the volume charge would be changed thereby.  
10 The volume charge, however, influences the ion-optical  
properties of the mass spectrometer (focusing of the ions)  
and, therefore, has to be held constant in precision  
measurements of isotope ratios. This is another reason why  
a change of the gas inflow would be very inappropriate.

15

The object of the present invention is to create a process  
or an apparatus which allows an isotope-ratio analysis which  
is as precise as possible.

20

The process according to the invention is characterized in  
that, in the analysis of a component which has the greater  
concentration with respect to the carrier gas, the  
concentration of this component is reduced by supplying  
additional carrier gas. Accordingly, in the analysis of CO<sub>2</sub>  
25 in connection with helium as a carrier gas, the sample gas  
is diluted with additional helium. Thereby, the  
concentrations of the sample gases in the carrier gas can  
be approximated to one another, so that the negative  
effects different concentrations of the sample gases have  
on the precision of measurement can be avoided. The total  
30 gas inflow is practically not affected by the addition of  
helium, because it is determined exclusively by the  
throttling effect of the inflow capillaries in the mass  
spectrometer. If the sample or component to be analyzed  
contains CO<sub>2</sub> and N<sub>2</sub>, successive measurements are conducted  
35 in the mass spectrometer, for example a determination of  
the isotope ratio of the N<sub>2</sub> first, and a subsequent  
measurement of the CO<sub>2</sub>. Each measurement is compared to the



1 standard samples.

Known per se is the principle of an open split before the entry of the gases to be analyzed in the ion source of the mass spectrometer. A fraction of the gases emerging from a line is transferred almost under atmospheric pressure to a further line. The largest portion of the gases to be analyzed is discharged as excess and thereby displaces possible secondary air flows. Advantageously, the dilution with additional carrier gas takes place in the region of this open split. The additional carrier gas does not influence the pressure ratio and flow conditions. Merely the ratio of carrier gas and gas to be analyzed is changed, especially of helium and CO<sub>2</sub>.

15 The dilution appropriately takes place in such a manner that the concentrations of the gases to be analyzed (CO<sub>2</sub> or N<sub>2</sub>) become approximately equal. To be more specific, after dilution the quantity of CO<sub>2</sub> in the CO<sub>2</sub>-analysis corresponds to the quantity of N<sub>2</sub> in the N<sub>2</sub>-analysis. For this reason the isotope-ratio analysis can be carried out with very high precision.

25 Starting out from an apparatus according to the preamble of the independent apparatus claim, the apparatus according to the invention is characterized in that a further supply line (dilution line) is provided, via which a further gas, in addition to the other gases emerging from the other supply lines, can be supplied to the throttle line. This apparatus makes it possible to carry out the above-mentioned process.

35 Further features of the invention are to be found in the subclaims and the description. Exemplary embodiments of the invention are explained in detail hereinafter by means of the drawings. In these:

1      Fig. 1      shows a diagrammatic representation of a system  
for conducting an isotope-ratio analysis,

Fig. 2 shows an enlarged detail of Fig. 1, namely a  
5 so-called open split in an embodiment according  
to the invention,

Fig. 3 shows an open split for the demonstration of the movement of the capillaries,

Fig. 4 shows the basic structure of the open split according to Fig. 3,

Fig. 5 shows a further embodiment of an open split in a representation similar to Fig. 2,

Fig. 6 shows a variation in a representation similar to Fig. 5.

The system shown in Fig. 1 is provided for conducting an isotope-ratio analyses by mass spectrometry. Two different embodiments are explained by means of the same figure. The point of departure is a gas chromatograph 10 (GC). A component of the sample contained therein and separated from the other components, for example an amino acid, is supplied to a combustion oven 14 via a line 12 and is oxidated therein. The combustion products resulting therefrom are separated in time via a gas supply line 16 in a second gas chromatograph 17 designated "Tr" for the separator in Fig. 1. Finally, the combustion products are supplied to a so-called open coupling (open split) 18 of the ion source of a mass spectrometer 20 (MS) comprising a multiple collector. For the analysis of CO<sub>2</sub>, for example a double collector can be employed, that is to say one collector each for the ions with the mass number 44 (C12) and 45 (C13), respectively. This type of analysis - without the second gas chromatograph 17 - is known as IRM-GCMS (Isotope-Ratio-Monitoring Gas-chromatography-Mass

1 Spectrometry) or as GC-IRMS (Gas-chromatography Isotope  
Ratio Mass Spectrometry). Corresponding to the schematic  
representation in Fig. 1, further details necessary for the  
analysis, for example valves or additional supply lines,  
5 are not shown if they are not directly related to the  
invention.

In another, very important application, a so-called element  
analyzer (EA) 22 or CHN-analyzer is employed instead of  
10 structural components 10, 12, 14, 17. A combustion oven and  
a GC are integrated in the EA. For example solid samples  
are fed into the EA and burned therein. Gases which are  
formed during combustion are separated in time, emerge one  
after another and thus can be fed one after another, via a  
15 supply line 24, to the line 16 which is connected to the  
open split 18.

The open split 18 is shown in more detail in Fig. 2 and  
takes the form of a small coupling tube 26 open at one side  
20 with a closed bottom 28 and an open end face 30. The gas  
emerging from the gas chromatograph or the combustion oven  
is piped into the region of the bottom 28 via a supply line  
16 with a corresponding opening 32. The gas is discharged  
via an opening 34 of a snifting or throttling line 36 which  
25 leads to the mass spectrometer, said opening 34 being  
located approximately centrally relative to the height of  
the small tube 26 (above the opening 32). The object is to  
determine the isotope ratios for carbon and nitrogen in the  
gases  $\text{CO}_2$  and  $\text{N}_2$  contained in one or various samples.  
30 Accordingly, two supply lines 38, 40 are provided for  
reference samples with exactly defined isotope ratios of  
the mentioned gases. Openings 42, 44 of the supply lines  
38, 40 also end inside of the small coupling tube 26.

35 In connection with the invention particular emphasis is  
given to a further supply line, namely a dilution line,  
which has an opening 48 that ends in the small coupling  
tube 26. Additional carrier gas can be supplied by this

1 small coupling tube 26.

For controlling the gas inlet into the opening 34 by  
varying immersion of the lines 46, 38 and/or 40, said lines  
5 are axially moveable. A mechanical device provided for this  
purpose is outlined by appropriate levers 51, 51, 53 in  
Fig. 2. These can be operated separately or in groups, so  
that the corresponding openings 48, 42, 44 are variable in  
their distance to the opening 34 of the inlet capillaries  
10 (snifting line 36). In an idle position, the lines 38, 40,  
46 rest above the snifting line 36 until they are needed.

The above system serves for a successive analysis of  $N_2$  and  
 $CO_2$ . Thus, a gas sample containing  $N_2$  and  $CO_2$ , for example,  
15 is supplied together with helium as a carrier gas in a  
volumetric rate of flow of 60 ml/min via the line 16 in the  
position according to Fig. 2. The small coupling tube 26  
has an inner diameter of approximately 1 mm. The portions  
of the lines 16, 46, 38, 40, 36 which are inside the small  
20 coupling tube 26 are designed as capillaries in a  
correspondingly fine manner. The volume of the gas entering  
into the small coupling tube 26 via the opening 32 is such  
that all secondary air is displaced from the region of the  
bottom 28. Furthermore, gas which possibly emerges from the  
25 openings 48, 42, 44 in the position shown in Fig 2 does not  
reach the bottom area. Thus, the gas flowing into the  
opening 34 of the throttling line 36 is always only a  
fraction of the gas coming from the line 16. The throttling  
line 36 has a precisely defined cross-section so that under  
30 constant compression ratios a constant gas supply to the  
mass spectrometer is ensured.

At times, a reversal of the lines takes place in order to  
supply a reference gas. For example a nitrogen gas  $N_2$  with  
35 a known standardized isotope ratio can be supplied via line  
40. This is done by lowering the line 40 by operating lever  
53. As a result the opening 44 is located underneath the  
opening 34 so that the throttling line 36 is supplied with

1 a mixture of reference gas and helium. Expediently, this  
operation takes place in an interval in which no sample gas  
emerges from the opening 32 or in which the line 16 is  
pulled out up to a level above the opening 34. The  
5 alternation between the sample gas via the line 16 and the  
reference gas via the line 40 is repeated several times.

After the measurement of the nitrogen gas  $N_2$ , the  
measurement of carbon dioxide takes place. As before, the  
10 sample gas flows into the small coupling tube 26 via the  
line 16 similar to the above-described procedure. The  
introduction of a reference gas via the line 38 is carried  
out in the above-described manner by means of an  
appropriate lever 52 ( $CO_2$  with standard isotope ratio and  
15 helium as carrier gas) as well. The mass spectrometer is,  
accordingly, readjusted from the masses for nitrogen  
isotopes to the masses of carbon isotopes.

The reading of the mass spectrometer 20 depends on the  
number of ions of the supplied sample gas. In the analysis  
of organic compounds or compound mixtures normally much  
more  $CO_2$  is produced for the analysis than  $N_2$ , and supplied  
with helium as carrier gas to the mass spectrometer 20 via  
the open split 18. In other words, the quantity of gas  
25 flowing in through the throttling line 36 at first contains  
a very large proportion of helium, a fraction of  $N_2$  and,  
compared to the latter, a much larger proportion of  $CO_2$ . In  
order to attain a very high precision of measurement, the  
quantity of helium should possibly be equal relative to  
30 both gases. At the same time, an adjustment of the maximum  
 $CO_2$  value to the maximum  $N_2$  value is advantageous for the  
evaluation. For this purpose, a dilution with additional  
carrier gas takes place during the analysis of  $CO_2$ . For  
this purpose, a further quantity of helium is introduced  
35 into the small coupling tube 26 via the line 46. To control  
this quantity, the line 46 is axially moveable by means of  
the lever 51. Each time the opening 48 of the capillaries  
46 (line) immerses into the space underneath the opening 34

1 of the snifting capillaries 36, the sample gas emerging  
from the opening 32 is diluted with carrier gas. The gas  
which is passed into the capillaries and into the mass  
spectrometer via the opening 34 is thereby diluted until  
5 the proportion of helium relative to the  $\text{CO}_2$  is  
approximately equal to the proportion of helium as it was  
before relative to the  $\text{N}_2$ .

10 In a further embodiment, the control of the gas supply is  
attained, in addition to or instead of the variation of the  
depth of immersion of the individual lines by means of the  
levers 51 to 53, by a limitation of the gas flow in the  
lines themselves, for example by means of appropriate  
15 valves. The switching over from the sample gas in the  
analysis of  $\text{N}_2$  to a corresponding reference gas  $\text{N}_2$  can thus  
take place by throttling the line 16 and opening the line  
40. Both lines should end in the area of the bottom 28.  
Similarly, switching over to a reference gas  $\text{CO}_2$  in the  
analysis of  $\text{CO}_2$  can take place by throttling the line 16  
20 and opening the line 38, also with openings 32, 42 in the  
region of the bottom 28. Additionally, in this case, it is  
necessary to control the gas for dilution by turning on the  
line 46 or deeply immersing the line 46 when it is open.

25 An example for carrying out the movement of lines inside of  
a small coupling tube will be explained below by means of  
Figs. 3 and 4. A small coupling tube referred to as pipette  
54 (corresponding to the small coupling tube 26), is fixed  
to a stand 55. Also fixedly connected thereto is a cylinder  
30 56 of a piston-cylinder unit as well as a retaining plate  
57. The latter carries a support 58 for the accommodation of  
two capillaries 59, 60 (lines). These capillaries both  
reach into the pipette 54 with corresponding openings 61,  
62.

35

A piston 63 which can be drawn out of the piston-cylinder  
unit (cylinder 56) carries a retaining plate 64. A support  
65 is fixed thereto for the accommodation of a further



1 capillary 66. The piston is vertically adjustable by  
admitting compressed air to the piston-cylinder unit  
(flexible tube connection 67). Accordingly, the capillary  
66 is moved up or down in the pipette.

5 For the sake of clarity, only one moveable capillary 66 is  
shown in Figs. 3, 4. According to the invention, more than  
one capillary may be provided. For this purpose the  
capillaries may immerse into the pipette 54 in curved  
10 shape, corresponding to the capillaries 59, 60. For example  
so-called fused silica capillaries are both flexible and  
axially moveable.

In the example shown in Figs. 3 and 4, the capillary 59  
15 with an inner diameter of 0.1 mm is provided for the  
introduction of helium, if necessary in connection with a  
sample gas. The capillary 66 has an inner diameter of 0.05  
mm and is provided for the introduction of a reference gas.  
The capillary 66 ends in an opening 68 in an adjustable  
20 region, preferably between the openings 61, 62. Finally,  
the capillary 60 is provided as a sniffing line, that is to  
say as a line with an inner diameter of 0.05 mm which leads  
to the mass spectrometer.

25 In the present example, a pneumatic actuation is provided  
for the movement of the capillaries 66. Other actuations,  
for example electrical or hydraulic, are possible.

Figs. 5 and 6. relate to further embodiments of the  
30 invention. Fig. 5 shows a modification compared to Fig. 2,  
comprising a small coupling tube 70 which is open at both  
ends. The gas supply line 16, dilution line 46, throttling  
line 36 as well as the reference gas line 38 correspond to  
the lines shown in Fig. 2. Just as in Fig. 2, further lines  
35 may be provided in the embodiment according to Fig. 5, for  
example a further reference gas line. The small coupling  
tube 70 is open at an end face 72. The lines 46, 36, 38  
immerse on this side (dilution line, throttling line,

1 supply line). The opposite end face 74 is partly closed or  
has only a comparatively smaller inlet cross-section 76.  
The gas supply line 16 coming from the element analyzer 22  
enters the small coupling tube 70 via the decreased inlet  
5 cross-section 76. Similar to Fig. 1, a supply from a gas  
chromatograph with downstream combustion oven and  
separating device may also occur.

10 A control of the gas concentration entering the opening 34  
of the throttling line 36 is possible by longitudinal  
displacement of the individual lines, especially 16, 38 and  
46. Alternatively or additionally, the gas flows in the  
individual lines can be throttled or shut off. According to  
the embodiment of Fig. 5, an axial movability of the  
15 reference gas supply line 38 is preferred. The movability  
is indicated by a double arrow 78. In the position shown in  
the figure, the reference gas moves from the dilution line  
46 to the throttling line 36, if necessary, together with a  
gas volume. If the reference gas supply line 38 is moved to  
20 the right, practically no reference gas reaches the  
throttling line 36.

Fig. 6 shows an expanded embodiment compared to Fig. 5.  
Instead of one small coupling tube 70, according to Fig. 6,  
25 two small coupling tubes are provided, in particular a  
thicker small coupling tube 80 and a thinner small coupling  
tube 82, which enters the former. The latter is open at  
both ends. The small coupling tube 80 corresponds in its  
structure to the small coupling tube 70, but is thicker in  
30 diameter. The inner diameters of the small coupling tubes  
80, 82 are approximately 3 mm and 0.7 mm, respectively.  
Accordingly, the gas flow emerging from the opening 32  
splits in the ratio of the end faces of the tubes  
(approximately 8.5:0.5). The small coupling tube 80 thus  
35 has the function of a precoupling towards the small  
coupling tube 82. The reference gas and the additional  
helium carrier gas enter the small coupling tube 82 via the  
lines 38 and 46, are mixed in the small coupling tube 82



1 and then enter the throttling line 36. Only opening 32 is  
located in the thicker small coupling tube 80.

5 A particular advantage of this embodiment is the uncoupling  
of the reference gas supply from the gas supply via the  
line 16 (sample supply). If different quantities of CO<sub>2</sub> (or  
other gases) are supplied at different times, the  
cross-section of the line 38 is best only for a certain  
10 volumetric rate of flow. Without the described coupling of  
the two small tubes 80, 82, the line 38 would have to be  
replaced with another line with appropriate diameter each  
time. In the embodiment according to Fig. 6, surplus  
reference gas can emerge via the coupling between the two  
small tubes 80, 82. Moreover, there are further advantages.  
15 Under normal operation, according to the description of  
Figs. 1 to 5, significantly reduced consumptions of the  
reference gas and the auxiliary helium flow (line 46) can  
be attained. For controlling the reference gas supply, the  
volumetric flow rate is variably adjustable by means of the  
20 line 46, preferably between 0 and 20 ml/min. The opening 48  
is located closely in front of the end 84 of the small tube  
82 which is located inside of the small tube 80. The  
opening 34 is located approximately centrally in the small  
tube 82. A very small volumetric flow rate from the opening  
25 48 already causes a partial displacement of the sample gas  
emerging from the opening 32. The latter does not enter  
into the small tube 82, but, on the contrary, exits via the  
end face 72. As a result a dilution of the sample gas can be  
attained with significantly reduced carrier gas supply.

30

Just like in the embodiment according to Fig. 1 to 4,  
axial movements of the lines would be possible in this  
embodiment by levers not shown.

35

Approximately a third or one half of the thinner coupling  
tube 82 is located within the thicker small tube 80. The  
opening 32 is located at a distance in front of the end 84.  
The dimensions of the thinner small tube 82 correspond to

1 those of the small tube 70 or 54. The small tube 80 has  
approximately the same length but is substantially thicker.  
A throttle valve in the tubing 46 is designated by the  
reference numeral 86.

5

The small tubes 70, 80, 82 and the capillaries (lines 36,  
38, 46, 16) can be fixed and moved just as shown in the  
representation in Fig. 3.

10 Organic compounds may contain further elements in addition  
to carbon and nitrogen, for example sulphur. In this case,  
gaseous  $\text{SO}_2$  would result from the combustion. The  
corresponding isotope ratio can be determined in the  
described manner, just as the isotope ratios of further  
15 elements.

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**Process for the analysis of gaseous components by mass spectrometry**

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**C l a i m s :**

- 1      1.      Process for the analysis of several, especially two,  
gaseous components by mass spectrometry, the components  
being supplied, simultaneously or successively, with a  
carrier gas to a mass spectrometer, the first component  
5      having a different volume ratio relative to the carrier gas  
compared to the second component, characterized in that, in  
the analysis of a component which is provided in a greater  
ratio relative to the carrier gas, the concentration of  
this component is decreased by additional supply of carrier  
10      gas.
2.      Process according to claim 1, characterized in that  
the dilution with additional carrier gas is carried out in  
the region of an open split (18) known per se.

1        3.        Process according to claim 1 or 2, characterized in  
that the dilution with carrier gas continues until the  
concentrations of the gases to be analyzed, especially CO<sub>2</sub>  
and N<sub>2</sub> in the carrier gas helium, become approximately  
5        equal.

10       4.        Apparatus for the provision of gaseous samples for  
the analysis by mass spectrometry comprising a so-called  
open split (18), at least one supply line (16) as well as  
especially at least one reference gas supply line (38, 40)  
and a throttling line (36) which leads from the open split  
to the ion source of a mass spectrometer (20), where the  
gas can be fed to the throttling line (36) alternately from  
one of the supply lines (16, 38, 40) approximately under  
15       atmospheric pressure, characterized in that a further  
supply line (dilution line 46) is provided, via which a  
further gas can be fed to the throttling line (36) in  
addition to the gas emerging from one of the other supply  
lines (16, 38, 40) for dilution of same.

20       5.        Apparatus according to claim 4, characterized in  
that, in the region of the open split (18), an outlet  
opening (32) of the gas supply line (16) is disposed  
adjacent to an inlet opening (34) of the throttling line  
25       (36) in a manner known per se, and that in the region near  
the inlet opening (34) the dilution line (46) with its  
outlet opening (48) can be moved in and out.

30       6.        Apparatus according to one of the claims 4 or 5,  
characterized in that the reference gas supply lines (38,  
40) can each be moved in and out in the region near the  
inlet opening (34) of the throttling line (36).

35       7.        Apparatus according to one of the claims 4 to 6,  
characterized in that the open split (18) takes the form of  
a small coupling tube (26) preferably open at one end, into  
which the lines (16, 46, 38, 40) are inserted as  
capillaries from at least one open end face (30).

1     8.     Apparatus according to claim 7, characterized in  
that the capillaries of the dilution line (46) and/or of  
the reference gas lines (38, 40) are moveable in the  
longitudinal direction of the small coupling tube (26) and  
5     inside of same.

9.     Apparatus according to one of the claims 4 to 8,  
characterized by the following features:

10    a)     the open split has two small coupling tubes (80,  
82),

b)     a portion of the thinner small tube (82) is inserted  
in the thicker small tube (80),

15    c)     at least the throttling line (36), the dilution line  
(46) and the reference gas supply line (38) end in  
the thinner small tube (82),

20    d)     the supply line (16), from which the sample gases to  
be analyzed emerge, ends in the thicker small tube  
(80),

25    e)     the cross-sectional surface of the small tube (80)  
is substantially greater than, especially 10 - 20  
times the cross-section of the thinner small tube  
(82), so that the surplus gas volume from the small  
tube (82) can emerge from the open split via the end  
face (72) of the thicker small tube (80).

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**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(The Search report)**

Application number  
 GB 9324729.4

**Relevant Technical Fields**

- (i) UK Cl (Ed.M)      G1B (BCF, BCG); G1N (NCGK)  
 (ii) Int Cl (Ed.5)      G01N, H01J

Search Examiner  
 M R WENDT

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 16 MARCH 1994

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-  
 1-9

(ii) ONLINE DATABASES: WPI, CLAIMS, ANALYTICAL ABS

**Categories of documents**

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| <p><b>X:</b> Document indicating lack of novelty or of inventive step.</p> <p><b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p><b>A:</b> Document indicating technological background and/or state of the art.</p> | <p><b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.</p> <p><b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p><b>&amp;:</b> Member of the same patent family; corresponding document.</p> |
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| Category | Identity of document and relevant passages | Relevant to claim(s) |
|----------|--|----------------------|
|          | NONE                                       |                      |

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